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None

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C3V

(54) Nail-strengthening cosmetic compositions

(57) A cosmetic composition comprises an amount of glyoxal sufficient to strengthen nails in admixture with a substantially non-aqueous conventional nitrocellulose-based nail lacquer preparation. The nail lacquers can be clear and colorless or can have pigments therein. The preferred amount of glyoxal is about 0.001 to about 1.00 weight percent of the composition.

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## SPECIFICATION

## Nail strengthening compositions and method of using same

5 This invention relates to cosmetic nail strengthening compositions. The compositions may be clear or colored with conventional organic and inorganic pigments. The invention also contemplates a method of strengthening nails by applying the inventive compositions to the nails.

Many users or would-be users of nail polish have difficulty due to cracked, split or broken toe nails and finger nails. The cause of these conditions has been attributed to one of more of the following: the use of nail polish and/or nail polish remover, the use of soap or detergents, and/or a natural idiosyncrasy of the user.

Numerous nail preparations have been made which claim to strengthen nails by the action of chemicals contained in them. Nail hardening compositions in which the principal active component is formaldehyde in a concentration generally ranging from 4 to 15% have been proposed. See for example, U.S. Patent 3,382,151 (Knudein). However, the use of formaldehyde in cosmetics produces undesirable side effects, such as inflammation, hardening and/or formation of horn on adjacent skin areas. In addition, the formaldehyde has a rather dangerous toxic effect, especially on the nerve cells of the skin and the capillaries. Accordingly, the U.S. Food and Drug Administration considers any solution which contains more than 4% formaldehyde to be "a poisonous or deleterious substance."

Numerous nail strengtheners have been proposed to overcome the problems associated with using formaldehyde.

UK Patent 1,183,513 (issued March 11, 1970) discloses compositions for treating nails containing one or more mono-aldehydes containing at least two carbon atoms or polyaldehydes containing more than two carbon atoms. U.S. Patents 3,349,000 and 3,725,525 disclose that use of the reaction product of formaldehyde with thiourea imparts to native keratins, e.g., nails, higher elasticity and strength than do free aldehydes without producing any undesirable side effects. U.S. Patent 382,151 discloses the use of a nail strengthening composition containing a high concentration of formaldehyde modified by vegetable extracts.

French Patent 1,485,602 (Morelle) discloses nail polish compositions containing aqueous solutions of glyoxal in combination with acylated protein derivatives.

U.S. Patents Nos. 4,296,104, 4,296,130 and 4,447,469 disclose nail conditioner and nail polish compositions containing glyoxal, high concentrations of water in admixture with methylsulfonylmethane (MSM), dimethylsulfoxide (DMSO) and carbimide or urea. However, MSM is disclosed as the active ingredient and DMSO is described as accelerating the penetration of MSM and urea or carbimide into the tough nail material.

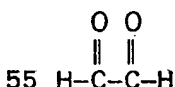
U.S. Patents Nos. 4,256,768 and 4,569,946 disclose topical application of dilute aqueous or alcoholic solutions of lower dialdehydes such as glyoxal to human tissue for treatment of gangrene, burns and raw, cut portions of the body during surgical excision of malignant tumors.

Nothing regarding nail strengthening compositions is recited.

There is a need for a nail strengthening composition that operates to strengthen nails efficiently and safely without causing the undesirable side effects experienced with prior art compositions.

The present invention is summarized as a cosmetic composition for strengthening nails comprising an amount of glyoxal effective for strengthening nails in a substantially non-aqueous conventional nitrocellulose-based nail lacquer preparation. The invention also provides a method of strengthening the nails which comprises applying to the nails a cosmetic composition comprising an amount of glyoxal sufficient to strengthen said nails in admixture with a substantially non-aqueous conventional nitrocellulose-based nail lacquer preparation, which preparation may be colorless or colored with conventional nail polish organic and inorganic pigments.

Glyoxal is a dialdehyde having the formula



and is commercially available as a 40% aqueous solution which also contains a polymerization inhibitor. Vacuum evaporation of the aqueous glyoxal solution leads to polyglyoxal, a trimer of glyoxal. Thermal depolymerization of polyglyoxal in the presence of drying agents yields unstable anhydrous monomeric glyoxal which must be used immediately. See for example G. Mattioda, et al., CHEMTECH, August 1983 pp. 478-481. Thus, while aqueous or anhydrous glyoxal may be used in the compositions and process of the present invention, the use of 40% aqueous glyoxal

Percentages of "glyoxal" in the compositions are based a 40% aqueous glyoxal solution, hence to obtain the percentage of dry glyoxal, multiply each percentage of "glyoxal" by 0.40. Of course the claims are intended to cover compositions prepared using solutions of glyoxal having different concentrations when said compositions contain the same amount of glyoxal on a dry basis.

The amount of glyoxal in the cosmetic composition of the present invention found effective for strengthening nails when added to a substantially non-aqueous conventional nitrocellulose-based nail lacquer preparation is about 0.001 to about 1.0 weight percent, preferably about 0.001 to about 0.25 weight percent, more preferably about 0.01 to about 0.25 weight percent of the cosmetic composition. By employing these amounts of glyoxal in said nail lacquer preparation in accordance with the present invention, nail strengthening is effected without the deleterious side effects associated with prior art formaldehyde-containing preparations.

The term "substantially non-aqueous" as used herein means less than about 1 weight percent water. With the exception of the small amount of water introduced by addition of glyoxal as a 40% aqueous glyoxal solution, no water should be intentionally added in the preparation of the cosmetic compositions of the present invention. However, the solvents and other components of the conventional nitrocellulose-based nail lacquer preparations need not be completely anhydrous for use in the cosmetic compositions and process of the present invention, provided the final composition is substantially non-aqueous as defined in this paragraph.

Conventional nitrocellulose-based nail lacquer preparations have been found useful in the present invention. Typical suitable conventional nitrocellulose-based nail lacquer preparations include:

Nitrocellulose (7-25%, more preferably 10-18%, and most preferably 12-16%),  
secondary resins (5-15%),  
plasticizers (2-8%), and  
solvents (55-80%, more preferably 60-80%).  
Other optional ingredients include:  
Thickening and suspending agents,  
UV light masking and suncreening agents,  
Colorants, and  
Decorative materials.

Nitrocellulose is the primary film-former used in the typical nail lacquer preparation and should have a viscosity value (R/S Value) of from 1/4 to 5/6 seconds (enabling the manufacture of cosmetic nail strengthening compositions that flow readily and are capable of producing a film with sufficient gloss in one application), and be perfectly neutral, for free acid may damage the finger nail and destroy the pigments used in tinting the nail lacquer preparation.

Typical suitable secondary resins compatible with nitrocellulose include most natural resins such as Benzoin, Dammar, Ester gum, Pontianac Sandara or Shellac and any synthetic resin such as the alkyd, acrylate- and methacrylate-based resins, polyester resins (Lipo Rez resins) and formaldehyde sulfonamide resins (Santolite resins). Santolite resin in combination with acrylate copolymer resins, is a preferred secondary resin. Other secondary resins include: nylon, available under the tradename of Versamid 930 from Henkel, Inc., Teaneck, NJ 07666, acrylates copolymer resins, available from Rhom and Haas Co., Philadelphia, PA 19105, under the tradename of Acryloid B-66, and styrene/acrylate/acrylonitrile copolymers, available from Dow Chemical U.S.A., Midland, MI 48640.

Typical suitable plasticizers include blown castor oil, camphor, raw castor oil, dibutyl phthalate and tricresyl phosphate. Use of a combination camphor and at least one or two other plasticizers, normally dibutylphthalate and/or sucrose acetate isobutyrate is conventional.

UV light masking agents used in clear nail lacquer compositions to mask the yellow color caused by discoloration of the nitrocellulose resin include pigments such as D&C Violet #2.

Typical suitable sunscreening agents include esters of para-aminobenzoic acid and substituted para-aminobenzoic acid, e.g., octyl dimethyl PABA; certain esters of salicylic acid, e.g., homomethyl salicylate; certain benzophenone derivatives, such as benzophenone-1 or -3; and the esters of para-methoxycinnamic acid, e.g., octyl methoxycinnamate.

The compositions of the present invention may also include thickening and suspending agents for the colorants. Typical suitable thickening and suspending agents include stearalkonium Hectorite, a reaction product of Hectorite (one of the montmorillonite minerals that are the principal constituents of bentonite clay) and stearalkonium chloride [a quarternary ammonium salt of the formula,

Typical suitable decorative materials include aluminum polyester terephthalate, available under the tradename Bril Chrome Silver from Meadowbrook Inventions, Bernardsville, NJ 07924; acrylates copolymer and polybutene terephthalate and ethylene/vinyl acetate copolymer available under the tradename Crystalina from Meadowbrook Inventions; Silver available under the tradename Silver from Presperse, Inc. So. Plainfield, N.J. 07080; decorative pearl available under the tradename Mearlmaid from Mearl Corp. NY, NY 10017; mica; titanium dioxide coated mica; bismuth oxychloride and guanine.

The solvent combination found suitable in conventional nitrocellulose-based nail lacquer preparations consists of an alcohol, such as ethanol or iso-propyl alcohol which is used to wet the nitrocellulose, together with an active solvent such as n-, sec- or iso-butyl acetate or ethyl acetate and an aromatic hydrocarbon diluent such as toluene or xylene. Other typical suitable solvents are found on pages 991-994 of "Nail Preparations" by Henry J. Wing, Chapter 49, pp. 983 to 1110, in "The Chemistry and Manufacture of Cosmetics", Second Edition, Volume IV edited by M. G. deNavarre, Continental Press, 1975, Orlando, Florida which is hereby incorporated by reference.

The conventional nitrocellulose-based nail lacquer preparation may be clear or colorless, i.e. unshaded or shaded. The shaded product may contain insoluble organic and inorganic colorants together with small proportions of titanium dioxide. The organic colorants should be selected from an FDA approved list of certified pigments and dyes; the inorganic pigments should conform to the FDA specifications with respect to heavy metal content. A listing of the opaque and transparent colorants is given on pp. 997-998 of "Nail Preparations" cited hereinabove.

The process of the present invention consists of strengthening finger or toe nails, by applying to the surface thereof using a conventional cosmetic composition such as described above or in the examples.

The following examples further describe and illustrate formulation of representative unshaded and shaded nitrocellulose-based nail lacquer preparations. All of the mixing operations of the examples were performed at room temperature.

The nitrocellulose was obtained from Hercules, Inc., Wilmington, DE 19899; the toluene sulfonamide/formaldehyde resin tradenamed Santolite resins from Monsanto Chemical Co., St. Louis, MO 63116; benzophenone-1 is a UV sunscreensing agent from BASF Wyandotte Corp., Parsippany, NJ 07054; isostearic hydrolyzed animal protein is a conditioning agent available under the tradename Crotein IPX from CRODA, NY, NY 10010; polyester resins available under the tradename Lipo Rez resins from Lipo Chemicals, Inc. Paterson, NJ 07504; and stearylkonium Hectorite is a thickening and suspending agent available from NL Chemicals Division of NL Industries, Highstown, NJ 08520.

The suppliers of other ingredients used in the following illustrative examples are well known and can be found, e.g. in CTFA Cosmetic Ingredient Dictionary, Third Edition, 1982, N.F. Estrin et al., eds., published by The Cosmetic, Toiletry and Fragrance Association, Inc., 1110 Vermont Avenue, N.W., Washington, D.C. 20005.

#### EXAMPLE 1 Colorless Nail Lacquer Composition

Ingredient	Weight %	
Butyl Acetate	26.00	
Toluene	20.00	
Nitrocellulose R/S 1/2 sec.	14.00	
Isopropyl Alcohol	5.00	
Toluene Sulfonamide Formaldehyde Resin	10.00	
Ethyl Acetate	19.599	
Camphor	0.50	
Benzophenone-1	0.10	
Nylon	0.10	
Acrylates Copolymer	0.10	
Sucrose Acetate Isobutyrate	4.00	
Polyester Resin	0.50	
Glyoxal	0.001	
D&C Violet No. 2, (0.01% solution)	0.10	
Total	100.000	

lose, benzophenone-1, camphor and sucrose acetate isobutyrate. To the stirred homogeneous mixture so formed, add nylon, acrylates copolymers, polyester resin and continue stirring until a homogeneous mixture is reformed. Continue stirring and add the isopropyl alcohol, D&C violet #2, remaining half of ethyl acetate, and glyoxal. Fill into bottles.

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**EXAMPLE 2***Colorless Nail Lacquer Composition*

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	<i>Ingredient</i>	<i>Weight %</i>	
10	Butyl Acetate	18.26	10
	Toluene	25.40	
	Nitrocellulose R/S 1/2 sec.	14.00	
	Isopropyl Alcohol	1.00	
15	Toluene Sulfonamide Formaldehyde Resin	10.00	15
	Dibutyl Phthalate	4.00	
	Ethyl Acetate	25.60	
	Camphor	0.99	
	Benzophenone-1	0.10	
20	Nylon	0.10	20
	Acrylates Copolymer	0.10	
	Glyoxal	0.25	
	D&C Violet No. 2, (0.01% solution)	0.10	
	Isostearic Hydrolyzed Animal Protein	0.10	
25			25
	Total	100.000	

Following the procedure of Example 2 except add the dibutylphthalate to the mixture containing nitrocellulose and add the isostearic hydrolyzed animal protein to the mixture containing nylon.

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**EXAMPLES 3 AND 4**  
**Colored Nail Polish**

5	<b>Ingredients</b>	<b>Weight %</b>		5
	<b>Part A</b>	<b>Example 3</b>	<b>Example 4</b>	
	Toluene	25.10	25.45	
	Toluene Sulfonamide/Formaldehyde Resin	9.00	0.05	
	Butyl Acetate	25.33	25.66	
10	<b>Part B</b>			10
	Nitrocellulose R/S 1/2 sec.	14.00	14.00	
	Stearalkonium Hectorite	1.30	1.30	
	Benzophenone-1	0.10	0.10	
15	Dibutyl Phthalate	2.50	0.05	15
	Camphor	2.00	2.00	
	Polyester Resin	2.50	10.00	
	Sucrose Acetate Isobutyrate	2.50	2.50	
20	<b>Part C</b>			20
	Nylon	0.10	0.10	
	Acrylates Copolymer	0.10	0.10	
	Styrene/Acrylate/Acrylonitrile Copolymer	0.05	0.05	
25	<b>Part D</b>			25
	Ethyl Acetate	4.00	5.00	
	Isopropyl Alcohol	10.00	10.00	
	Butyl Alcohol	1.00	3.00	
	SD-Alcohol-3A	0.05	0.05	
30	Glyoxal	0.01	0.01	30
	<b>Part E</b>			
	Titanium Dioxide	0.20	0.04	
	D&C Red No. 7 Calcium Lake	0.05	0.09	
35	Iron Oxides	0.08	0.05	35
	D&C Red No. 6 Barium Lake	0.02	0.20	
	Ferric Ammonium Ferrocyanide	0.01	—	
	Bismuth Oxychloride, 11%	—	0.20	
40	<b>Total</b>	<b>100.00</b>	<b>100.0</b>	40

To an appropriate stainless steel kettle equipped with a high shear stirrer, charge the ingredients in Part A and stir until a homogeneous mixture is formed. Slowly add to the so formed mixture the ingredients in Part B. Stop stirring and cover kettle to prevent evaporation of solvents and hold so formed homogeneous mixture for 10 hours. Remove cover, stir and add the ingredients of Part C. To the so formed homogeneous mixture, add the ingredients in Part D. To the homogeneous mixture so formed add the ingredients in Part E and stir until a homogeneous mixture is formed.

**50 CLAIMS**

1. A cosmetic composition for strengthening nails comprising an amount of glyoxal effective for strengthening nails in a substantially non-aqueous conventional nitrocellulose-based nail lacquer preparation.
2. The composition of claim 1 containing from 0.001 to 1 percent glyoxal.
3. The composition of claim 2 containing from 0.001 to 0.25 percent glyoxal.
4. The composition of any one of claims 1 to 3 wherein the substantially non-aqueous conventional nitrocellulose-based nail lacquer comprises.
  - (a) 7 to 25% nitrocellulose,
  - (b) 5 to 15% secondary resins,
  - (c) 2 to 8 plasticizers, and
  - (d) 55 to 80% solvents.
5. A method of strengthening nails comprising applying to the nails the composition of

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